Journal of Organometallic Chemistry 749 (2014) 327–334

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Tuning second-order nonlinear optical properties of the two-dimensional benzene/carborane compounds with phenyl carbazoles: Substituent effect and redox switch

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A R T I C L E I N F O

Article history:
Received 19 June 2013
Received in revised form
8 October 2013
Accepted 9 October 2013

Keywords:
Carborane
Two-dimensional
Redox
Second-order NLO property

A B S T R A C T

Density functional theory (DFT) calculations have been carried out to investigate the substituent effects and redox switching of the second-order nonlinear optical (NLO) properties of a series of the two-dimensional (2D) diaryl-substituted benzenes/carboranes. The calculated static first hyperpolarizabilities (β_{tot}) of the neutral compounds increase with replacing the central benzene with carborane, extending the π-conjugated bridge, and introducing an electron donor into carbazole moiety. Particularly, a dramatic enhancement of the β_{tot} values for the oxidized/reduced species is observed. The β_{tot} values of one-electron oxidized/reduced species for compound **3** are 14 times and 32 times as large as that of its neutral counterpart, respectively. Furthermore, the electronic structure analysis shows that the carbazole performs as an oxidized center and the benzene/carborane performs as a reduced center. Interestingly, the second-order NLO responses are two-dimensional in characteristic with the large off-diagonal tensor values. This work not only provides more penetrating insight into the second-order NLO properties of 2D benzene/carborane-based compounds, but also obtains an efficient approach for devising redox-switchable NLO materials.

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1. Introduction

Molecular nonlinear optical (NLO) materials are of considerable current interest because of their potential utility in emerging optoelectronics and photonics technologies [1–4]. Typical second-order NLO chromophores are one-dimensional (1D) π-conjugated compounds endcapped with donor (D) and acceptor (A) moieties. However, in recent years, the 2D V-shaped molecules have been regarded as new candidates owing to the significant NLO responses [5–7]. For example, the two-dimensional (2D) chromophores with large off-diagonal β tensor components exhibited better phase matching [8,9]. The 2D molecules can enhance the second-order NLO responses without undesirable visible transparency losses. Moreover, these 2D molecules can form transparent and phase-matched acentric crystal structures which exhibit large second-order NLO responses due to large off-diagonal β tensor components [10].

To date, molecular switches have been reported displaying changes in properties including luminescence [11], color [12], magnetism [13] and NLO properties [2,14]. Among them, the second-order NLO properties may be an attractive procedure that is used to explore the molecular switches. In the context of NLO properties, NLO switches have been achieved by redox [15–17], photoisomerization [18], and protonation/deprotonation sequences [19], and so forth. Some excellent theoretical works have been also performed to modulate the NLO response to produce NLO switching materials. As a pioneer, Coe et al. have reported the redox switching of quadratic NLO responses for various ruthenium (Ru) complexes [20,21]. A series of hyper-Rayleigh scattering (HRS) experiments with Ru-based complexes indicated that $Ru^{II} \rightarrow Ru^{III}$ oxidation caused β values to decrease substantially. There are also redox-switchable second-order NLO properties of tetrathiafulvalene (TTF) derivatives coming from the reports of Liu et al. [22,23].

Molecular and polymeric boron-containing compounds display optical and electronic properties that make them particularly attractive for use in functional materials [24,25]. These compounds can exhibit sizable second- and third-order NLO properties [26–33], strong two-photon excited fluorescence (TPEF) and large two-photon absorption (TPA) cross-sections [34,35]. Boranes and borides compounds indeed have spanned a large area of chemistry owing to their aesthetically appealing structures, unique bonding features and the formation of cages and clusters [36–38]. As a

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http://dx.doi.org/10.1016/j.jorganchem.2013.10.018

subclass of boranes, the field of icosahedral carboranes has developed extensively over recent years. Since the discoveries of carborane clusters, relentless efforts have been made to understand their unique cage structures and electronic properties [39–43]. Carboranes are known as the inorganicanalogs of benzene [40,44], which ten boron and two carbon atoms constitute a 12 vertex icosahedral geometry. In particular, the icosahedral boron-carbon clusters (o-carborane (o-$C_2B_{10}H_{12}$)) exhibit three-center two-electron bonds and three-dimensional conjugated electrons that confer high chemical and thermal stability [40,45]. Icosahedral carboranes linked organic groups fulfill many requirements of optical nonlinearities, thus, some theoretical studies on the NLO properties of carborane have been stimulated [3,46–52]. Recently, Wee and coworkers [53] have synthesized V-shaped carborane-based compounds with phenyl carbazoles, 1,2-bis(4-(*N*-carbazolyl)phenyl)-ortho-carborane and 1,2-bis(4-(*N*-carbazolyl)biphenyl)-ortho-carborane. The analogous benzene molecule 9,9′-(1,1′:2′,1″-Terphenyl-4,4″-diyl)dicarbazole was also prepared [54]. Moreover, their photophysical properties have been systematically investigated. Importantly, it has been proved that these compounds undergo redox processes which provide the possibility for the molecular NLO switches. Furthermore, carborane leads to considerable hyperpolarizabilities owing to its strong electron-withdrawing character [55,56]. Up to now, there is a paucity of theoretical investigations on NLO properties for these V-shaped benzene/carborane compounds with phenyl carbazole groups, therefore a detailed understanding of the structure–property relationship for these V-shaped organic molecules containing benzene/carborane with phenyl carbazole groups is significant.

On the basis of above perspectives, we took the synthetic compounds **1**, **2** and **3** as NLO-phore and designed novel compound **4** by introducing donor groups to probe into the NLO properties (see Fig. 1). We performed DFT calculations on these V-shaped 2D compounds (D-π-A-π-D/A-π-D-π-A) to explore their second-order NLO responses. In addition, the redox switching character of NLO responses has been also investigated in detail. It is our expectation that this work may open a novel way to provide an ideal method for designing switchable high-performance 2D NLO materials.

2. Computational details

All calculations in the work were performed by using the Gaussian 09W program package [57]. The geometric structures of all compounds have been fully optimized using B3LYP/6-31g(d) level with no symmetry constraint [58,59]. To obtain more accurate geometries, basis sets effect has been taken into account with a larger basis set 6-31+g(d). Frequency calculations were carried out to verify the identity of each stationary point as a minimum. What is more, dichloromethane solution was applied in the optimization using the continuum solvation model (SMD) [60] involving nonelectrostatic interaction. The calculated geometric parameters and crystallographic data of compounds **2** and **3** have been shown in Table S1 (Supporting information). The results indicate that calculated geometric parameters of compounds **2** and **3** at the B3LYP/6-31g(d)/6-31+g(d) level are in reasonable agreement with reported experimental data. Additionally, a comparison between 6-31g(d) and 6-31+g(d) basis sets has shown that the addition of diffuse function has a slight influence on the structure of compounds **2** and **3**. Thus, considering the computational cost, 6-31g(d) basis set has been selected to optimize the studied compounds.

The time-dependent density functional theory (TDDFT) method is one of the most successfully and extensively used methods to calculate the excitation energies in quantum chemistry because of its efficiency and accuracy [61,62]. To choose suitable calculated methods, the electron absorption spectra of compounds **2** and **3** were simulated using TD-B3LYP, TD-PBE1PBE, TD-B3PW91 and TD-CAM-B3LYP methods with 6-31+g(d) basis set associated with SMD in dichloromethane solution, utilizing the previously optimized ground-state geometries. The calculated absorption wavelengths and relevant experimental results have been listed in Table S2 (Supporting information). According to the results, PBE1PBE functional predicts the UV–vis spectra of compounds **2** and **3** very well, even though it shows a deviation of 4–5 nm with respect to the experimental data. Furthermore, for the calculation of redox potentials for oxidative and reductive species, the solvent effects of dichloromethane were taken into account by the SMD model which is the recommended choice for computing ΔG of solvation [63,64].

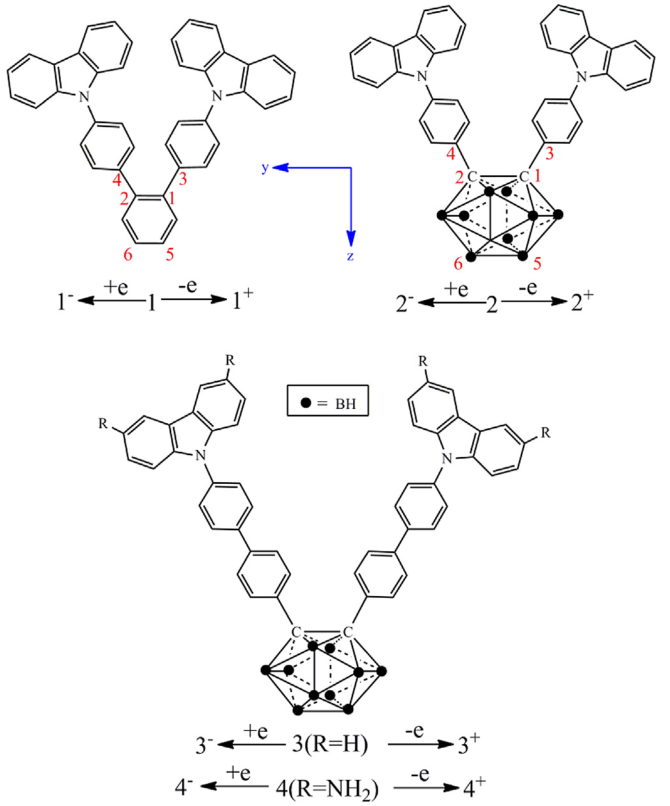

Fig. 1. The calculation model for the studied compounds.

The response of a molecule to a homogeneous static electric field can be represented by the following two Taylor expansions [65]:

$$E(F) = E^0 - \sum_i \mu_i^0 F_i - 1/2 \sum_{ij} \alpha_{ij} F_i F_j - 1/3 \sum_{ijk} \beta_{ijk} F_i F_j F_k - 1/4 \sum_{ijkl} \gamma_{ijkl} F_i F_j F_k F_l + \ldots \qquad (1)$$

where E^0 is the energy of the molecule in the absence of an electric field, μ_i^0 is its permanent dipole moment, α_{ij} is the dipole polarizability, and β_{ijk} and γ_{ijkl} are the first and second hyperpolarizablities, respectively. As implied by this, the polarizabilities can be obtained by employing derivatives of the energy or dipole moment with respect to the incident electric field. In this article, the first hyperpolarizability (β_{tot}) of the studied compounds was calculated by analytic third energy derivatives, which is more efficient and less expensive than numerical derivatives [66]. PBE1PBE and B3PW91 functionals were employed to calculate the

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